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RESEARCH ARTICLE

Biogenic silica contents of Lake Qinghai sediments and its environmental significance

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Abstract Changes in the levels of biogenic silica (BSi%) in lake sediments have been widely used in order to study lake productivity and palaeoclimatic changes. However, the provenance of biogenic silica (BSi) needs to be investigated for each lake, especially for large lakes, as does the relationship between levels of BSi and relevant environmental factors. In this study, we measured the percentage of BSi contained in lake sediments, river sediments, and surface soils within the Lake Qinghai catchment, and compared the quantities and shapes of diatoms and phytoliths before and after the extraction processes. The results suggest that BSi in lake sediments is primarily derived from endogenous diatoms; therefore, BSi levels can be used to reflect the changes in primary productivity within the lake. Further comparisons showed that on long-term timescales, the variations in BSi% are generally consistent with those in total organic carbon (TOC) and grain size, reflecting the dominant impacts of precipitation on primary productivity in Lake Qinghai. On short-term timescales, however, the relationship between BSi% and TOC and that between BSi% and grain size are not clear or stable. For example, BSi% sometimes covaried with grain size, but it was sometimes out of phase with or even inversely related to grain size. We speculate that both climate and environmental processes, such as the dilution effect, influence short-term BSi% and its related environmental significance. As a result, BSi% should be used selectively as an indicator of climatic changes on different time scales.

Keywords biogenic silica, environmental significance, Lake Qinghai, precipitation

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1 Introduction

Biogenic silica (BSi) is a type of amorphous silica derived primarily from diatoms, radiolarian, sponges, and other siliceous organisms. BSi in ocean/lake sediments contains unique information about the spatial and temporal distribution of primary productivity, and it has been widely used in studies of palaeoceanography and palaeoclimate changes (Broecker and Peng, 1982; DeMaster et al., 1991, 1996; Broecker, 1994; Ragueneau et al., 2000; Ye et al., 2003).

Previous studies paid more attention to BSi in marine sediments, while BSi in lake sediments has received more attention in recent decades. The results suggest that in most cases, the BSi in lake sediments can be used to indicate climate and environmental changes on different time scales and over a wide geographical area (Carter and Colman, 1994; Colman et al., 1995; Xiao et al., 1997; Wang et al., 2000; Russell and Johnson, 2005; Fritz et al., 2010). However, as the geographical settings, biogeochemical processes, and climatic conditions are quite variable between different lakes, the environmental significance of BSi in each specific lake is different, especially on different time scales. In addition, the provenance of BSi in lake sediments, especially in some large lakes, is not clearly documented. As a result, it is necessary to study the BSi in lakes systematically, and to investigate its provenance and environmental significance in each particular instance.

Lake Qinghai is located in the northeastern Qinghai-Tibet plateau, and is affected by the Asian winter monsoon, the Asian summer monsoon, and the westerly. It is sensitive to global climatic changes and has received worldwide attention (Lister et al., 1991; LZBCAS, 1994; Yu and Kelts, 2002; Henderson et al., 2003; Ji et al., 2005; Shen et al., 2005; Liu et al., 2011). Research on BSi in

Lake Qinghai sediments would be helpful in understanding the climatic changes and ecological responses in this area. However, the provenance of BSi in the sediments of Lake Qinghai, the temporal and spatial variations in BSi%, and the corresponding environmental significance of these variables have not been well studied. In this study, we measured the levels of biogenic silica (BSi%) of different end-members in the Lake Qinghai catchment, and discussed possible sources of BSi in lake sediments and the potential of BSi% as an indicator of climatic changes.

2 Background and methods

2.1 Geological setting and background

Lake Qinghai (36°32′–37°15′N, 99°36′–100°47′E; 3,200 m a.s.l.) is the largest closed, semi-saline inland lake in China, with a surface area of approximately 4,400 km^2 and a catchment area of approximately 29,660 km^2 (LZBCAS, 1994). Mean annual precipitation is approximately 319–395 mm (LZBCAS, 1994), and more than 80% of this falls between June and September (Xu et al., 2010a). Mean annual evaporation is about 800–1,000 mm, and more than 60% of the total amount occurs between June and September (LZBCAS, 1994). The temperature around Lake Qinghai varies between −10.4°C and −14.7°C in January and between 10.4°C and 15.2°C in July, with a mean annual value of −0.7°C (Xu et al., 2010a). The tributaries are asymmetrically distributed. Among them, the Buha river is the largest one and contributes approximately 48.3% of the runoff of the entire catchment area. The bedrock of the catchment consists primarily of metamorphic and acid igneous rocks. Water chemistry in the Lake Qinghai catchment has been systematically investigated previously (Xu et al., 2010b), with some fundamental parameters that are listed in Table 1. Total dissolved solids and pH values of the lake water are generally high due to strong evaporation (Xu et al., 2010b).

The previous survey shows that diatoms are abundant in the lake (particularly in the summer season, about 6.3×10^4 cells/L) (LZIGCAS, 1979), and constitute a predominant fraction of the composition of whole algae, about 88.92% in summer (LZIGCAS, 1979). As a result, the diatoms biomass should be parallel to the total biomass and, if so, can be used as an indicator of the primary productivity of the lake.

2.2 Sampling

We collected riverbed grabbing samples near the riverbed margin of seven rivers within the Lake Qinghai catchment in August, 2010, and in May, 2011 (see the sampling sites in Fig. 1). These rivers are the Buha river, the Shaliu river, the Hargai river, the Heima river, the Daotang river, the Quanji river and the Ganzi river. Surface soils from the uppermost 1–2 cm were also collected (grab sampling) around the lake.

We had previously collected surface lake sediment cores (2007) using a self-designed gravity corer and had conducted a preliminary study of the BSi contents in three short cores (QH0707, QH0708, and QH0711; see Liu et al. (2010) for details). In this study, we collected another short core (July 2010, 85 cm long, labelled QH10A; Fig. 1) and cut it into slices every 1 cm for further examination and comparison.

2.3 Measurements of bulk BSi

There are several methods for measuring BSi% in sediments (DeMaster, 1981; Mortlock and Froelieh, 1989), the most common of which is the wet alkaline extraction technique for lake sediments (Mortlock and Froelieh, 1989). We previously carried out a series of experiments to optimize the BSi extraction process in Lake Qinghai sediments (Liu et al., 2010). In this series, BSi% was measured following our previously optimized method: 1) Samples for BSi measurements were freeze-dried and ground to pass through a 150 micron mesh sieve; 2) BSi was extracted using 0.5 mol/L Na_2CO_3 in an 85°C water bath for 7 hours; and 3) BSi% was measured (using ammonium molybdate as the chromogenic reagent) using an ultraviolet visible spectrophotometer (Shimadzu UV2550, Japan) at 680 nm (see Fig. 2 for details).

Table 1 The chemical parameters of waters from different end-members in Lake Qinghai catchment

Water chemistry	Lake water	River water	Groundwater	Rainfall water
$Na^+/(mg\cdot L^{-1})$ a)	4406.11	14.03	49.52	0.92
$K^+/(mg\cdot L^{-1})$ a)	165.36	1.17	1.91	0.78
$Ca^{2+}/(mg\cdot L^{-1})$ a)	22.50	37.50	43.80	13.10
$Mg^{2+}/(mg\cdot L^{-1})$ a)	852	20.40	13.90	0.88
$TDS/(mg\cdot L^{-1})$ a)	15564	532.02	300.66	68.11
pH a)	9.11	8.05	8.05	<8
Dissolved $Si/(mg\cdot L^{-1})$ b)	4.76 ($N=8$)	0.84 ($N=40$)	5.15 ($N=25$)	\

Data sources: a) Major cation concentrations and pH values from our previous measurements (Xu et al., 2010b); b) Data that were measured in this study. "*N*" is the number of measured samples.

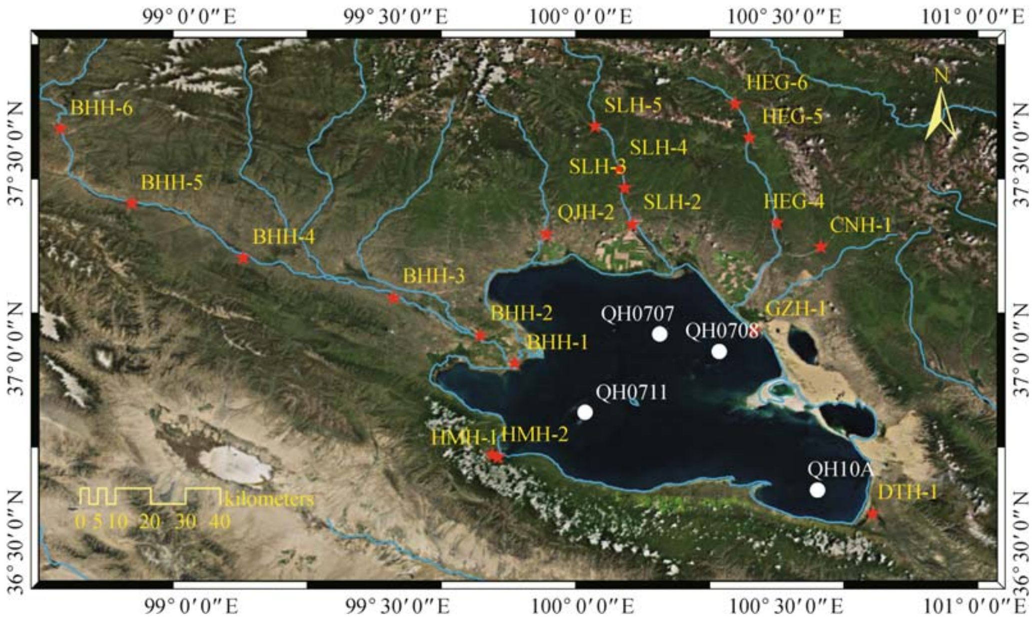

Fig. 1 Sampling sites of the surface soils, river sediments, and lake sediment cores within the the Lake Qinghai catchment. The red stars indicate the sampling sites for surface soils and river sediments, while the white dots indicate sampling sites of surface lake sediment cores.

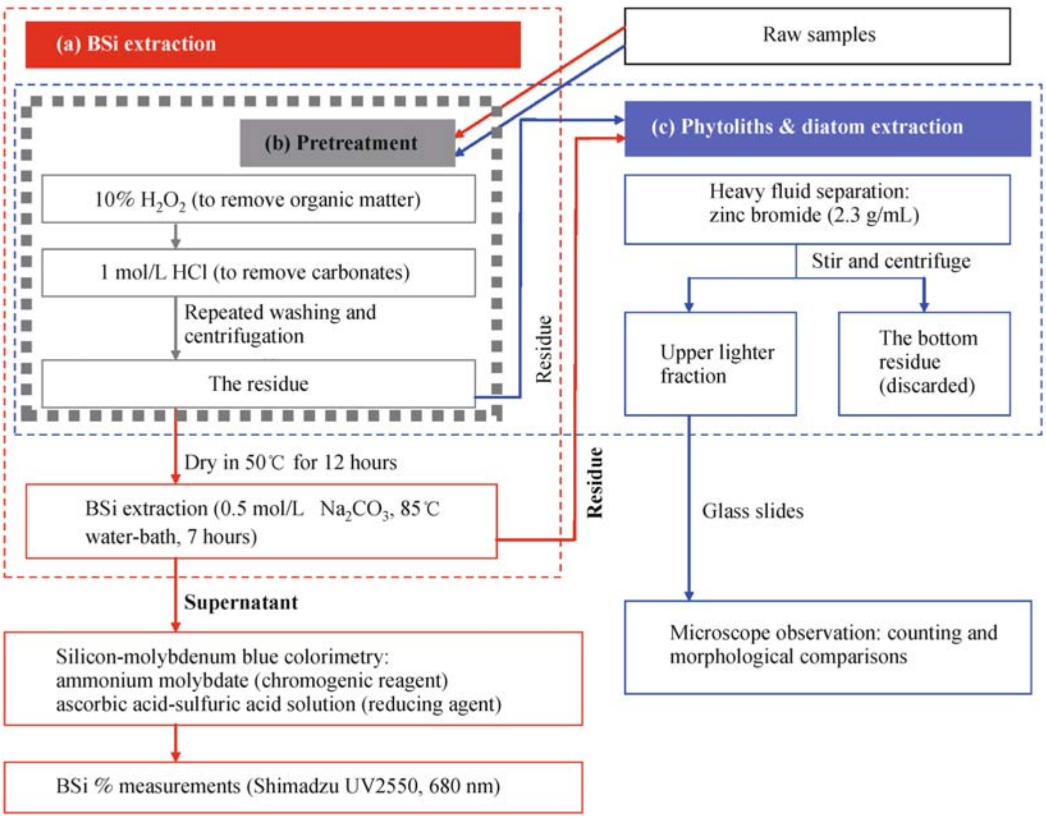

Fig. 2 Procedures for the measurement of BSi% and the extraction of phytoliths and diatoms.

Frame (a) (red dotted) shows the full procedure for BSi extraction, while frame (c) (blue dotted) shows the full procedure for the extraction of phytoliths and diatoms. Frame (b) (grey dotted); overlapping with frames (a) and (c)) shows the pretreatment processes for the extraction of BSi, phytoliths, and diatoms.

2.4 Phytoliths and diatoms extraction

Sponge spicules and phytoliths derived from both aquatic and terrestrial plants may also contribute to the inventory of BSi. Some agricultural crops around Lake Qinghai, including brassica, oats, and highland barley, contain phytoliths and therefore may potentially contribute BSi to the lake sediments. We therefore need to determine whether the BSi of the lake sediments was of endogenous origin or was produced by the terrestrial plants. We developed two approaches to accomplish this objective. First, we compared the BSi% in lake sediments, river sediments, and surface soils (see below). Secondly, we compared the shapes of phytoliths and diatoms by witness before and after the BSi extraction process, with the purpose of examining the degree of dissolution of the phytoliths and diatoms. The phytoliths and diatoms were extracted using the heavy liquid flotation method, as described by Kelly (1990), which consists of the following steps: 1) oxidation of the organic matter using 10% hydrogen peroxide, 2) dissolution of carbonates using 15% hydrochloric acid at 90ºC, and 3) densimetric separation of phytoliths and diatoms from the residue using a zinc bromide solution with a density of 2.3 g/cm^3 (see the extraction processes in Fig. 2).

2.5 Morphological comparisons

Lake sediments, river sediments, and surface soils were selected for comparison. All of the samples were divided into two groups. In the first group, the samples were subjected to the BSi extraction processes (including pretreatment and BSi extraction processes), and the residues were then used for phytolith and diatom extraction. In the other group, the raw samples were subjected to the pretreatment processes only and then used for phytolith and diatom extraction (Fig. 2). The extracted phytoliths and diatoms (light fractions) were then transferred to glass slides. The phytoliths and diatoms were counted at 400× magnification with an Olympus light microscope (LM), and photographs of one phytolith body and one diatom valve were obtained with a scanning electron microscope (Zeiss EVO, Germany) (see the results in Fig. 3).

2.6 Measurements of grain size and TOC

To investigate the environmental significance of BSi% in lake sediments, we also measured the levels of total organic carbon (TOC%) and the grain size of the QH10A core for comparison. The grain size was measured using a laser diffraction instrument (Malvern 2000, England), with an error of less than 3%. The total organic carbon (TOC)

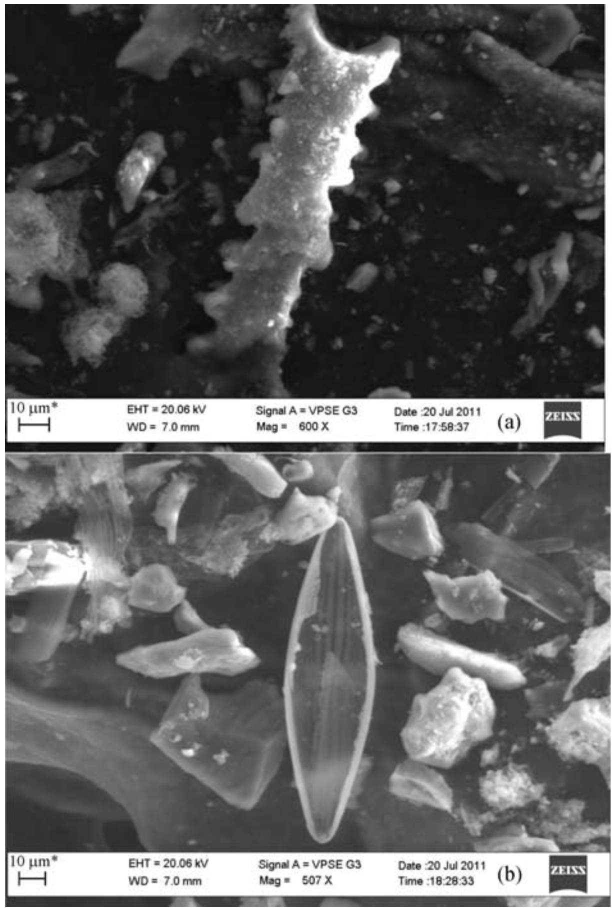

Fig. 3 Scanning electron microscope (SEM) photographs of phytoliths (a) and diatoms (b) in Lake Qinghai sediments. The sediments are from a mixed 30 cm long surface core (100°10.999′ E, 36°47.713′N; water depth: ~25.3 m).

was measured (after removal of carbonates) using an elemental analyser (Elemental Analyzer vario EL III, Germany), with an error of less than 0.2%.

3 Results and discussion

3.1 The source of BSi in Lake Qinghai sediments

The microscope counts showed the following: 1) The raw lake sediments (without Na_2CO_3 extraction) contained a large number of diatoms (Table 2), far more than the river sediments and surface soils (Table 2). Most of the diatoms in the lake sediments were relatively intact (see photographs in Fig. 3(a)). 2) After the alkaline extraction, almost no intact diatoms were detected in either the lake and river sediments, or surface soils. This result suggests that the alkaline treatment has a high BSi extraction efficiency, and that the diatoms are almost fully dissolved by alkali. 3) Phytoliths are almost undetectable in river and lake sediments, but some phytoliths do exist in surface soils (see photographs in Fig. 3(b)). These results agree with the fact that there are some phytolith-containing plants living around the lake, as mentioned above. 4) The quantities of phytoliths in surface soil samples, river sediments, and lake sediments are not significantly different before and after the alkaline extraction, suggesting that the weak alkali used in the BSi extraction processes does not dissolve the phytoliths, or does so to a very limited extent. These results suggest that the contribution of phytoliths to the bulk BSi% of the lake sediments is rather weak. Therefore, the primary contributor to BSi in lake sediments is most likely to be diatoms from the lake.

3.2 The BSi contents of surface soils, river sediments, and lake sediments

Comparisons of the BSi% of surface soils and river sediments show that the BSi% of surface soils is generally slightly higher than that of river sediments, in the major rivers within the Lake Qinghai catchment (Table 3), which can be attributed to the washing effect of the river water. However, the BSi% of river sediments is much higher than that of the surface soils in the Heima river (Table 3), possibly because the Heima river receives much more domestic sewage, which favors the blooms of diatoms, especially near the estuary areas.

A comparison among the average BSi% of the surface soils (0.8%), river sediments (0.7%), and lake sediments (2.3%) (Fig. 4) shows that the BSi% of the lake sediments is much higher than the BSi% of the river sediments and surface soils. This result suggests again that the endogenous diatoms in the lake are the main source of BSi in lake sediments.

3.3 Comparison between BSi and TOC

3.3.1 Comparison between BSi and TOC on long-term time scales

Measures of total organic matter (TOC) in lake sediments are widely used to indicate both catchment biomass input and lake primary productivity (Meyers, 1997; Xu et al., 2006). In the boreal summer over the northeastern plateau of Tibet, higher precipitation, concomitant with higher temperatures, creates favorable hydrological conditions and a rich nutrient supply, which is expected to increase biomass in the catchment and primary productivity within the lake, and eventually result in increased sedimentary TOC. Therefore, higher levels of TOC in lake sediments are correlated with higher precipitation, and vice versa. The coherence between TOC in Lake Qinghai and precipitation at Delingha, reconstructed using tree ring width, strongly supports such a relationship (for details, see Xu et al., 2006, 2007).

For a vertical core, even though the diatoms are easily dissolved when the pH is higher than 9, the dissolved BSi is still preserved within the lake sediments (or within the porewater). Although the dissolved BSi may be moveable, its migration should be neglected for a relatively long term timescale. This is analogous to the use of porewater Cl^- concentrations to indicate changes in salinity in vertical sediment cores (e.g., Branchu et al., 2010). As a result, the BSi% in the sediments of Lake Qinghai can be used to indicate climate and environmental changes indirectly. Warm and wet climate conditions are favorable for the growth of diatoms and should therefore correspond to higher BSi% (and vice versa). As shown in Fig. 5, the BSi% and TOC% of the core QH10A show good coherence. Our preliminary data suggest that core QH10A covers a time span of approximately two millennia. This result suggests that on centennial or even longer time scales, the variations of BSi% in Lake Qinghai sediments are consistent with those of TOC%. Therefore, the long-term variations in BSi% can be used as an indicator of precipitation. This response of BSi% to climate change observed during this study is similar to that of BSi in the Huguangyan Maar lake in the Leizhou peninsula (Wang et al., 2000), where the Asian summer monsoon also prevails in the warm season.

3.3.2 Comparison between BSi and TOC on short-term time scales

We compared the BSi% and TOC% of four short surface cores, namely, QH0707, QH0708, QH0711, and QH10A,

Table 2 Counts of phytoliths and diatoms in surface soils, river sediments, and lake sediments before and after the BSi extraction processes

Sample	Before alkali treatment		After alkali treatment	
	Diatoms	Phytoliths	Diatoms	Phytoliths
BHH-2 river sediment	A few integrated diatoms	Very few phytoliths	No observed integrated diatoms	Very few fragments of phytoliths
BHH-2 surface soil	Few diatoms	A few phytoliths (approximately 50 on one slice)	Few diatoms	A few phytoliths (approximately 54 on one slice)
HEG-4 surface soil	Few diatoms	A few phytoliths (approximately 30 on one slice)	Few diatoms	A few phytoliths (approximately 18 on one slice)
QH lake sediment	A large number of integrated diatoms	Few phytoliths	No observed integrated diatoms	Few phytoliths

Table 3 The BSi content of surface soils, river sediments, and lake sediments in the Lake Qinghai catchment

Sample numbers	BSi/%	Sample numbers	BSi/%
HEG-4 surface soil	0.8	HEG-4 river sediment	0.7
HEG-5 surface soil	0.6	HEG-5 river sediment	0.8
HEG-6 surface soil	0.6	HEG-6 river sediment	0.4
SLH-2 surface soil	1.1	SLH-2 river sediment	0.7
SLH-3 surface soil	0.7	SLH-3 river sediment	0.7
SLH-4 surface soil	0.7	SLH-4 river sediment	0.5
SLH-5 surface soil	0.8	SLH-5 river sediment	0.6
BHH-1 surface soil	0.9	BHH-1 river sediment	0.8
BHH-2 surface soil	0.8	BHH-2 river sediment	0.6
BHH-3 surface soil	0.9	BHH-3 river sediment	0.5
BHH-4 surface soil	0.7	BHH-4 river sediment	0.6
BHH-5 surface soil	0.5	BHH-5 river sediment	0.5
BHH-6 surface soil	0.8	BHH-6 river sediment	0.6
HMH-1 surface soil	0.9	HMH-1 river sediment	1.2
HMH-2 surface soil	0.7	HMH-2 river sediment	1.1
DTH-1 surface soil	0.6	DTH-1 river sediment	0.6
QJH-2 surface soil	0.7	QJH-2 river sediment	1.2
GZH-1 surface soil	1.1	GZH-1 river sediment	1.0
Surface soil average	0.8	River sediment average	0.7
Lake sediments average	2.3		

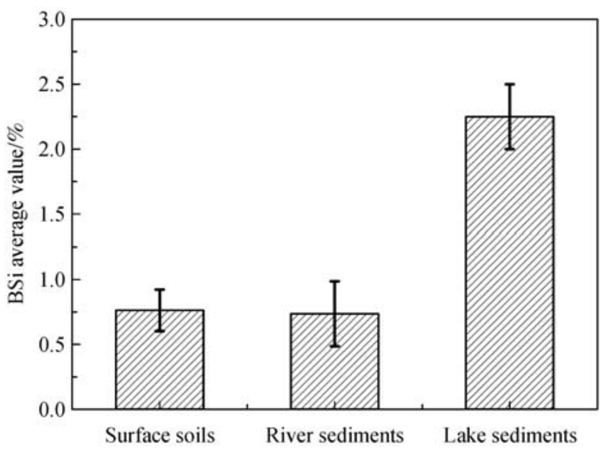

Fig. 4 The average levels of BSi in surface soils (0.8%), river sediments (0.7%), and lake sediments (2.3%) of the Lake Qinghai catchment. The bars indicate the standard deviation of the data.

to examine their relationships on short-term time scales. The results show that the relationships on short-term scales are not as strong as they are on long-term scales (Fig. 6). Such differences may be ascribed to both the climatic changes and the local environmental processes which influence the BSi-TOC relationship on short term time-scales. The long-term variations of TOC% and BSi% mask the details and exhibit broad consistency, while the short-term variations amplify the details and reveal a more variable relationship (also see below).

3.4 Comparison between BSi and grain size

The grain size of lake sediments has been widely used to reflect changes in, lake hydrology, runoff, and the intensity of atmospheric circulation, etc. However, interpretations of the climatic significance of grain size are quite variable. One generally accepted explanation for this variability is that the hydrodynamics of lake water exert a strong influence on the distribution of grain size. For example, levels of coarse and fine grains can indicate the enhancing and weakening of lake water hydrodynamics, respectively (Xiao et al., 2012, 2013). During a dry period, as the lake level falls and the lake area shrinks, the sampling site is closer to the bank, so more coarse particles are transported and deposited. On the other hand, in a wet scenario, the lake level rises, the area of the lake increases, and the sampling site is farther from the bank. Under these conditions, fewer coarse particles are brought, resulting in a smaller grain size of the lake sediment. Therefore, in summary, coarse sediments indicate a lower lake level and drier climate, and vice versa. This pattern may hold for relatively shallow and small lakes and/or for prolonged time scales (e.g., the glacial/interglacial time scales).

However, for a time span of approximately the past

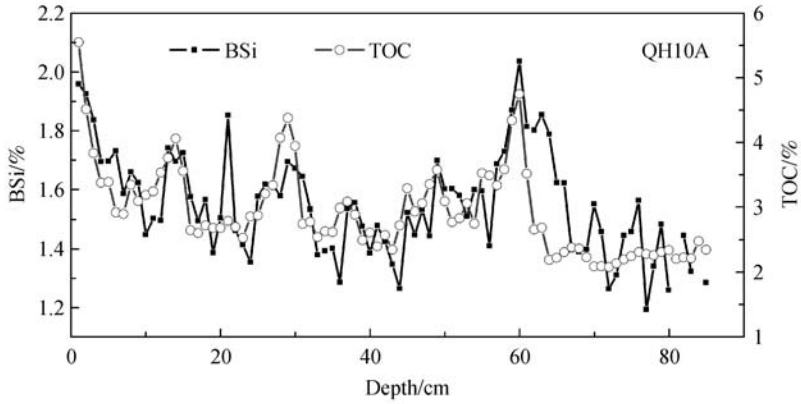

Fig. 5 Comparison between BSi% and TOC% of core QH10A.

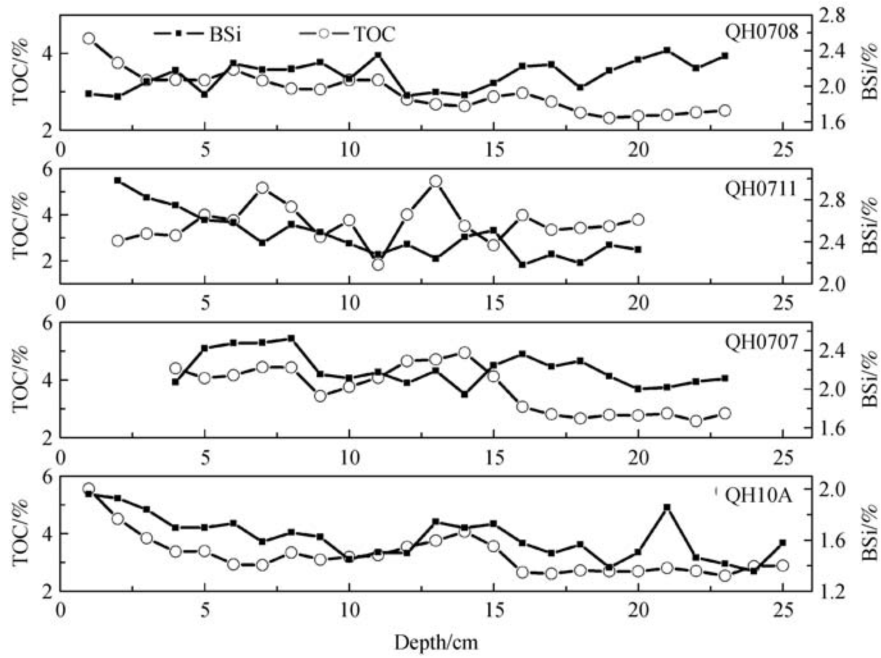

Fig. 6 Comparison between the BSi% and TOC% of core QH0708, core QH0707, core QH0711, and core QH10A (0–25 cm).

2,000 years, the variations in lake level are not very large. This means that, during this time period, the changes in distance from the sampling site to the lake shoreline should be subtle compared with the distance itself, especially for large lakes such as Lake Qinghai. As a result, we propose that the centennial variations in grain size over the past 2,000 years are more likely attributable to riverine runoff, and are thus also related to climate changes. Higher precipitation and the concomitant higher temperature in the study area were hypothesized to lead to increased runoff (including increased snowmelt) and, therefore, to the transport of more and larger particles into the lake. On the other hand, cold and dry conditions were expected to correlate to the transport of smaller particles. As a result, on centennial scales over approximately the past 2,000 years, the larger grain sizes of lake sediments may be related to higher precipitation, and smaller grain sizes may be related to drier conditions. Under this scenario, the grain size of lake sediments was expected to be positively correlated with TOC% and BSi%.

As shown in Fig. 7, the long-term trends between BSi% and grain size (volume-weighted mean grain size in our study) are broadly consistent with our hypotheses; suggesting again that the long-term variation in BSi% can be used as an indicator of precipitation. However, this pattern is not as stable on short-term time scales. For example, from approximately 61 cm to the bottom of the QH10A core, the relationship between BSi% and grain

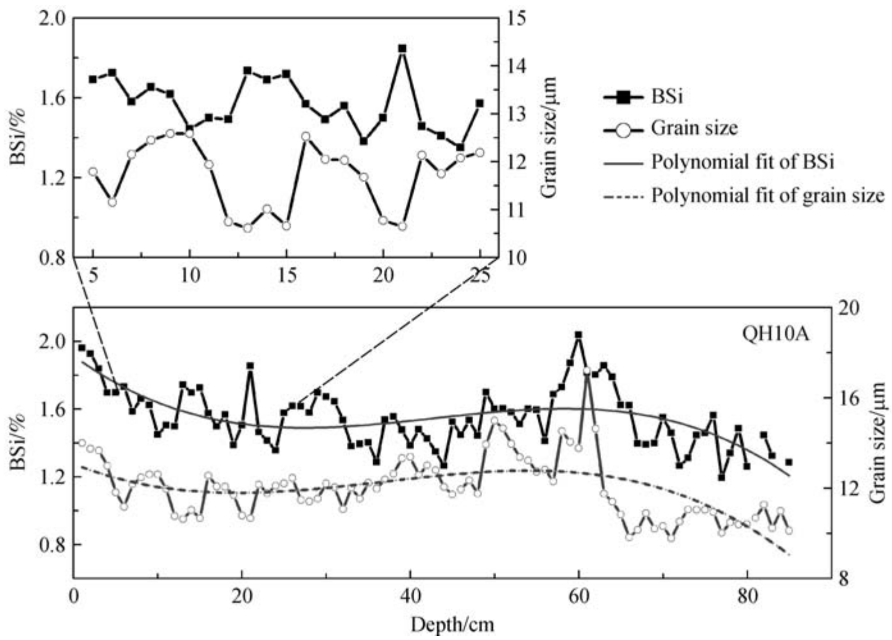

Fig. 7 Comparison between BSi% and grain size of core QH10A.

size is not clear; from approximately 39 to 60 cm, there seems to be a generally positive correlation on decadal scales. On the other hand, from a depth of approximately 38 cm to the surface, the decadal variations in BSi% and grain size seem to be inversely related. These different patterns on short term timescales may be closely related to different climatic conditions and limnological processes.

4 Conclusions

We measured the BSi% in the surface soils, river sediments, and lake sediments of the Lake Qinghai catchment, and compared the quantity and morphologies of diatoms and phytoliths before and after the extraction experiment. The results show that BSi in the lake sediments that were sampled is mainly derived from the diatoms of Lake Qinghai. Comparing BSi% with TOC% and grain size, we found that the variations in BSi% are broadly synchronous with those of TOC% and grain size on long-term time scales, suggesting that precipitation is a common long-term determinant of BSi%, TOC%, and grain size. On short-term time scales, however, BSi% has no significant and obvious correlation with either TOC% or grain size. This result suggests that on short-term time scales, BSi% is influenced by complex factors such as climate or dilution effects. Our work suggests that the BSi% in sediments of Lake Qinghai can potentially be used to study long term climatic changes, while for short term timescales this measure should be used with caution.

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